

Duquesne patent

METHOD FOR CONTINUOUS PROCESSING OF FLUIDS USING
SUPERCRITICAL FLUIDS AND MICROWAVE ENERGY

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Abstract

A method for the continuous processing of fluids is based on mixing the fluid with a supercritical fluid and applying microwave energy. The process focuses on the selective solubility of the desired components into supercritical fluid and deemphasizes the influence of the contaminating components of the fluid to be processed. The process of the present invention is particularly advantageous to the recycling of fluids, such as oil, wherein the process is carried out by statically mixing a waste material with a supercritical fluid to dissolve oil from the waste material. Microwave energy is applied prior to, at the same time, or after the static mixing step. Thereafter, undissolved components are allowed to settle and the dissolved oil is separated from the supercritical fluid. Various apparatus for carrying out the method are also disclosed.

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Description

METHOD FOR CONTINUOUS PROCESSING OF FLUIDS USING
SUPERCRITICAL FLUIDS AND MICROWAVE ENERGY
BACKGROUND OF THE INVENTION

Field of the Present Invention

This invention relates to a method for continuously processing fluids (liquids or gas) using supercritical fluids and microwave energy. The method has many applications, but

it fundamentally deals with the separation of industrial fluids into sub-components based on the different solubility of the components in supercritical fluids. Microwave energy complements this process in that the microwaves break up emulsion, adsorption and molecular interactions of specific sub-components of the fluids, and it also is used to directly induce energy driven reactions and synthesis and derivitization in an accelerated manner.

Description of the Prior Art

The present invention is particularly useful in the recycling of petroleum products.

For example, used lubricating and hydraulic oils are generated by a number of industries, including automotive and commercial shops, large industrial manufacturing facilities, marine facilities and airline and railroad maintenance departments. Used oils are considered hazardous wastes and are heavily regulated. It is the contamination of these oils with water and waste products that prevent their continued use. Generators of used oils are responsible for cradle to grave management of these waste streams and, in most cases, contract with used oil recyclers to remediate or dispose of the waste under the laws that regulate the transport, processing and destruction of the various components that make up these particular waste streams.

Currently, on-site remediation of these waste streams proves to be quite costly. The generators must contract with firms that have special expertise in reclaiming these waste streams as an on-site service.

As an alternative, used oil recyclers can pick up oil from generators for transportation back to a plant for processing. After the oil is processed it can be resold as burning fuel. This process of treating used oils is complex, costly and time consuming and produces waste components that require further remediation. Further, these used oils that are burned as fuel oils result in the original value of the oil being greatly reduced. Through purification to achieve a state as close to original quality and value as possible, much of the value of these recycled materials can be recovered. It has been the lack of a purification process of sufficient quality that has prevented the direct reuse or higher value use of these materials.

Currently, batch supercritical fluid systems are commonly employed in separation and purification and are fundamentally limited due to the specific technology and design approach. Prior art exists that employs batch systems for purification using supercritical fluid systems that are at very high pressure, and that employs vessels of large volume; these systems are extremely expensive and less efficient than the present invention. Other prior art continuous supercritical fluid systems use a counter flow technology. This technology uses a very complex long vertical column where feed material flows from top to bottom and supercritical carbon dioxide fluid flows from bottom to top, selectively dissolving specific components from the feed liquid. This particular system is very inefficient and relies on a large surface area on a wire mesh inside the column to strip off lighter components from the feed liquid. It requires many temperature sensors and

complex controls, and it has very limited flow efficiency. Consequently, the liquid is usually required to be recycled several times to sufficiently extract desired components.

Microwave energy has been used in the prior art for a number of purposes. For example, Nikola Smardzija, in U. S. Pat. No. 4,853,507, describes an apparatus for deemulsification of liquids using microwave energy as radiated into an applicator section consisting of a wave guide section that has a taper applicator element of low dielectric constant material separating the wave guide section into a radiation input void end and a larger volume liquid-filled output end; whereby an emulsion under pressure is input to the wave guide section output end adjacent the applicator element to undergo radiation and convection heating and subsequent separation into constituent components.

In U. S. Patent No. 4,582,629, Wolf teaches that an oil and water emulsion can be more rapidly separated when exposed to electromagnetic radiation in the range of from 1 to 300 millimeters. The treatment can be in conjunction with other separating and heating devices such as skimmers, gun barrel treaters, heater treaters, and the like. See also U. S.

Patent Nos. 5,911,885 entitled Application of Microwave Radiation In A Centrifuge For The Separation Of Emulsion And Dispersions and 5,914,014 entitled Radio Frequency Microwave Energy And Method To Break Oil And Water Emulsions.

Carbon dioxide has been used to facilitate the separation of emulsions. For example, in U. S. Pat. No. 5,435,920 Elfie Penth teaches a process for cleaving spent emulsions such as cooling lubricants by means of carbon dioxide under pressure, and if necessary, heat in an economic and environmentally friendly manner. The emulsion of cooling lubricant is saturated under pressure with carbon dioxide and is heated and/or cooled until cleavage is achieved. Above the cleavage temperature, a floating water-poor oil phase quickly forms above an oil-poor aqueous phase.

The effects of supercritical carbon dioxide have also been studied. For example, in Yamaguchi et al., Volumetric Behavior of Ethyl Esters Related to Fish Oil in the Presence of Supercritical CO₂, the 4th International Symposium on Supercritical Fluids, May 11-14, Sendai Japan (1997), pp. 485-488, supercritical CO₂ was used for the separation and fractionation of certain components of fish oil. The experimental apparatus included a static mixer in a water bath, and was a batch process. Another example of the use of supercritical CO₂ is Nagase et al., Development of New Process of Purification and Concentration of Ethanol Solution using Supercritical Carbon Dioxide, Id. at pp. 617-619. The experimental apparatus included a pre-heater and a static mixer in an air bath. The experimental system was used for solubility studies and not for continuous processing of fluids.

Notwithstanding advances in the art, the need still exists for a process for treating fluids, particularly the recycling of oil, which can be used on-site, which utilizes a continuous flow system and that proves to be cost effective and environmentally friendly.

SUMMARY OF THE INVENTION

This invention relates to a method for the processing of fluids-solutions, suspensions, gases, solvated solids and emulsions. The process uses a continuous supercritical fluid microwave-enhanced procedure. A fluid to be processed is mixed in the same direction with a supercritical fluid. The process focuses on the selective solubility of the desired components in a supercritical fluid and de-emphasizes the influence of the contaminating components of the fluid to be processed. The processed components may dissolve selectively in supercritical fluid according to the pressure and temperature of the supercritical fluid. Supercritical fluid can be directly mixed with the sample or sequentially introduced after a heating treatment using microwave or thermal energy.

According to one embodiment of the invention, at the same time the mixture passes through a reactor transparent to microwave energy for continuous processing, the unique reactor contains mixing elements for statically mixing the fluids. The processed fluid components may separate into individual components due to microwave energy or undergo chemical reactions enhanced by the microwave energy. Microwave energy may be applied initially at low pressure or at high pressure in this process, or it can be substituted with thermal energy, as required.

At least two separation vessels are employed for the continuous flow and the separation of dissolved and undissolved components from the fluid to be processed in the supercritical fluid. The supercritical fluid parameters can be continuously modified to alter the solubility and selectivity of the solvated components. The dissolved components can be phased out according to their solubility in supercritical fluid (s), inside separation vessels on a continuous basis, and after depressurization at different temperatures and pressures. The gas or liquid supercritical fluid is then recycled on-line, pressurized and heated to supercritical fluid conditions continuously and again used.

The present invention is also directed to an apparatus for recycling reusable components from a fluid to be processed comprising: a reactor comprising static mixing elements for mixing the fluids to be processed and a supercritical fluid, the reactor being transparent to microwave energy; a microwave energy source configured to supply microwave energy to the reactor; and at least two separation vessels.

Additionally, the present invention is directed to an apparatus for recycling reusable components from fluids to be processed comprising: a microwave energy source configured to supply microwave energy to the fluid to be processed; a reactor comprising static mixing elements for pressurizing and mixing the fluid to be processed and a supercritical fluid; and at least two separation vessels.

Additionally, the present invention is directed to an apparatus for recycling reusable components from fluids to be processed, comprising: a reactor comprising static mixing

elements for mixing the fluids to be processed and a supercritical fluid, the reactor being transparent to thermal energy; a thermal energy source configured to supply thermal energy to the reactor; and at least two separation vessels.

One benefit of the present invention is that it is ideally suited for cleaning up marine oil spills and processing crude oil sludge. Therefore, the present invention is ideally suited to play a major role in improving the environment.

Another benefit of the present invention is that it can be used in a number of processes including the purification of lubricating oil, gasoline and diesel fuel, used oils, transformer oils and other similar petroleum based samples. Additionally, the present invention can be used in the fractionation of citrus oils into its components to produce natural sweeteners. The present invention can be used in the purification of pharmaceuticals such as copolymers to remove lighter molecular weight components and by-products. The present invention can also be used in the production of well-defined polymer fractions of very narrow molecular weight ranges, as well as in the fractionation of fats and natural oils in foods and nutrition.

Another benefit of the present invention is that it is a continuous process. The present invention does not require the use of demulsifier to breakup water-oil complexes. This eliminates a costly and time-consuming step, although demulsifiers can be added to the present invention. Because the process is continuous, it can be automated such that operating labor is dramatically reduced, and the present invention is less dependent on the education level of the operator requiring less preliminary testing and judgement.

Another benefit of the present invention is the elimination of the need for a large holding tank, previously used in prior art systems for 36 hours/batch. The new process depends on physical constants, that is, solubility parameters of the oil molecules or fluid being treated, not on the contaminants, which are orders of magnitude more soluble and constant compared to the contaminants. These qualities are reflected in the quality control and quality assurance of the final product.

Another benefit of the present invention is that it minimizes waste components that require further remediation. For example, when the present invention is used to process a petroleum product, the amount of water and other residues in the starting material does not alter the quality of the final product or its fundamental process procedure. The present invention minimizes the production of the rag layer, that is, undissolved oil residue and water layer. This reduces or eliminates another cost element, that is, disposing of the rag layer.

Another benefit of the present invention when used to process waste oil is that it produces higher quality clean oil than the prior art, which oil can be sold at a much higher value than traditional used oils which are typically sold as #2 burning fuel. The final product of the present invention can be very clear and resembles clean engine oil, rather than the black #2 burning fuel. Therefore, the present invention could play an important role in the

future conservation of the hydrocarbon resources. The present invention can also remove chlorinated compounds from the final product.

Another benefit of the present invention is that this system can be easily scaled or adapted to both volume and flow. Energy is conserved in the process as part of the fundamental design. Flexibility in integration with other components such as microwave components of the system is enhanced due to this design. The present invention can be scaled down to be dedicated for some specific applications. For example, it can be used on a small scale to recycle well-defined used oil, such as on merchant or navy ships, military engines and other such applications. The clean product can be used as clean engine oil after making up some of the depleted additives.

The present invention is also so compact that it can be used as a mobile processing system making it possible to take the present invention to the source. This is a strategic advantage and one that may introduce a new paradigm in this field. Because of this compact nature it is also possible to integrate the purification into other mechanical systems to continuously purify oil and solvent components.

The fundamental nature of the present invention is more amenable to real time application in conjunction with other processes. The continuous operation and the fewer requirements for a holding tank, allow the process to be applied in other than tank or tanker batches and permit a new flexibility. By adding one module to the existing system it can also be used as a dedicated application for cleaning of oil contaminated solids such as metal parts, machinery or rags with the oil directed to the oil purification process.

Those and other advantages and benefits of the present invention will become apparent from the Detailed Description of the Preferred Embodiment herein below.

BRIEF DESCRIPTION OF THE DRAWINGS

For the present invention to be easily understood and readily practiced, the invention will be described, for purposes of illustration and not limitation, in conjunction with the following figures wherein:

FIGURE 1 is a system used to practice the method of the present invention;

FIGURE 2 is a simplified version of the system used to practice the method of the present invention as shown in FIGURE 1, wherein a high-pressure microwave is used;

FIGURE 3 is a variation of the system used to practice the method of the present invention wherein a low pressure microwave is used; and

FIGURE 4 is a variation of the system used to practice the method of the present invention wherein thermal heat is used.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

FIGURE 1 represents all of the major elements of a system I capable of practicing the method of the present invention. The fluid to be processed is transferred from sample reservoir 2 by sample pumps 4 into microwave transparent reactor 10. Liquified gas is transferred from solvent reservoir 6 by solvent pump 8 and may be preheated to supercritical conditions by a preheater (not shown). Thereafter, it is input into microwave

transparent reactor 10. The fluid (liquid, suspension, or gas) to be processed is either mixed directly with the supercritical fluid upon entering microwave transparent reactor 10, or the fluids to be processed and the supercritical fluid may be sequentially introduced. Because the fluid to be processed and the supercritical fluid, collectively the fluids, travel together through the system

1 from this point on, the continuous process is referred to as a co-flow process.

The internal diameter and length of the fluid path within microwave transparent reactor 10 depends on the volume of the fluids per unit time. The fluid path within microwave transparent reactor 10 contains static mixing elements (not shown), which may or may not absorb microwave energy depending on the material of construction and placement in the system. Microwave energy, from microwave source 11, is absorbed by microwave transparent reactor 10 to provide a constant microwave energy absorber, thereby reducing the influence of the microwave absorbing character of the fluid being processed and to provide energy absorption control. The static mixing elements in the fluid path of microwave transparent reactor 10 cause massive turbulence during operation to ensure complete mixing of the various fluids inside the reactor and to mass transfer the solubilized components into supercritical, subcritical or liquid phase. Reactor 10 may take various forms, some of which are discussed in conjunction with FIGURES 2-4 herein below.

The supercritical fluid acts as a solvent, which selectively dissolves certain components of the fluid being processed. Table I is an example of some of the conventional supercritical fluids that are commercially available and may be used in the present invention.

All conventional solvents can be used as a co-modifier to enhance the solubility parameters of supercritical fluids. Modifiers (usually an organic solvent), usually increase the solvation power of the supercritical fluids. Modifiers may dissociate sample molecules by forming clusters around them. These clusters may dissolve more rapidly in supercritical fluids in comparison with sample molecules. Analog modifiers can make supercritical fluids more selective for certain types of components depending on their chemical structure. The analog modifier shares at least a common functional group with the component to be selectively solubilized by the supercritical fluids. By adding the modifier directly to the supercritical fluid, and monitoring their concentration on line, or by premixing modifiers with the fluids to be processed, the selectivity of the supercritical fluid can be "tuned" to the fluid being processed.

Table 1 Physical Parameters of Selected Supercritical Fluids
Critical

Fluid	T. (C)	Pc (atm)	g/ml	g/ml	g/ml	g/ml
CO ₂	31.3	72.9	0.47	0.96	0.93	(63.4 atm. 25 C)
N ₂ O	36.5	72.5	0.45	0.94	0.91	(sat. 0 C)
	0.64					(59 atm. 25 C)
NH ₃	132.5	112.5	0.24	0.40	0.68	(sat., -33.7 C)

0.60 (10.5 atm. 25 C) n-C5 196.6 33.3 0.23 0.51 0.75 (1 atm. 25 C) n-C4 152.0 37.5 0.23
 0.50 0.58 (sat., 20 C)
 0.57 (2.6 atm. 25 C)
 SF6 45.5 37.1 0.74 1.61 1.91 (sat., -50 C)
 Xe 16.6 58.4 1.10 2.30 3.08 (sat., 111. 75 C) CClzF2 111.8 40.7 0.56 1.12 1.53 (sat., -45.6
 C)
 1.30 (6.7 atm. 25 C) CHF3 25.9 46.9 0.52---1.51 (sat., -100 C)

At least two separation vessels 12,14 are employed for the continuous flow and the separation of dissolved and undissolved components from the fluid being processed and the supercritical fluid. Additional separation vessels may also be employed for the fractionation of dissolved components using isobaric or isothermal conditions according to their solubilities in the supercritical fluid at different densities. The undissolved components in the supercritical fluid are allowed to precipitate and settle out in first separation vessel 12. The dissolved components in the supercritical fluid then enter second separation vessel 14 from the top at a lower pressure and temperature. Under the new conditions the supercritical fluid becomes liquid or gas, as required. The previously dissolved components are no longer soluble and phase separation takes place, which results in the separation of these components to the bottom of second separation vessel 14. The gas may be condensed in condenser 16 and cooled down into liquid, or alternatively the liquid could be cooled. The resulting liquid is pressurized and heated into supercritical, subcritical or liquid before recycling back to solvent pump 8 for continuous operation. The purified liquid is drawn off in either first separation vessel 12 or second separation vessel 14 depending on its solubility in the supercritical fluid.

The system I of the present invention is usually closed during operation but may be open if recycling of the solvating fluid is not desired. The separated components of the fluid being processed are removed periodically from separation vessels 12,14 by opening valves

13,15, respectively, at the bottom of each separation vessel 12,14. The separated components of the processed fluid could alternatively be continuously drawn off in a controlled manner.

Temperature sensors 17 monitor the temperature of the fluids in reactor 10. That information may be relayed to a central control system 18 which may, in turn, control the microwave source 11. Another set of temperature sensors and controls 19 monitor the temperature of the fluids in the separation tanks 12,14. Temperature information is relayed to central control system 18 which may then regulate the temperatures in tanks 12,14. Those of ordinary skill in the art will recognize that pressure gauges, valves, and other devices will be needed to properly operate the system 1 shown in FIGURE 1. Such devices are well known in the art and have been omitted from FIGURE 1 for purposes of clarity.

FIGURE 2 represents a simplified system used to practice the method of the present invention, wherein microwave transparent reactor 10 is a high-pressure reactor. Microwave energy is used at the same time as mixing to energize larger molecular complexes, emulsions, and suspensions separating them into their individual components.

Ultrasonication device 30 may be installed on microwave transparent reactor 10 to increase mixing efficiency.

Ultrasonication in supercritical conditions can create sinusoidal compression/decompression waves inside supercritical reactor 10 to effectively mix the components. In addition as previously described, reactor 10 has static mixing elements which create massive turbulence.

The turbulence increases the efficient absorption of the microwave energy, by preventing shielding of fluid components. In one variation of the present invention, the static mixer is also a microwave absorber. This absorbing mixer makes the microwave absorption characteristics of the fluid being processed much less critical as the mixer acts as a constant that is more significant than most differences in the absorption characteristics of various fluid types. Also the temperature is more controllable as the static mixer provides a strong constant absorption and passes the thermal energy to the fluid being processed and the supercritical fluid. The heating of the fluids coupled with the rapid mixing of all of the fluids inside reactor 10 will insure maximum solubility and a phase transfer into the supercritical fluid of specific components depending on the components' solubility in the supercritical fluid at that pressure and temperature.

In FIGURE 2 the supercritical fluid being processed and microwaves are introduced essentially simultaneously and are all present during the process as it starts. This variation is important if separation of the components is required as soon as the emulsion is broken up by the microwave energy. Because disrupted phases and components are not usually stable in separated form in the original liquid, supercritical fluid is necessary to solubilize the individual components. The polar components are less soluble in supercritical fluid while the non-polar components are very soluble in the supercritical fluid.

FIGURE 3 represents mixing and microwave energy absorption by the fluid being processed at low (or lower) pressure in a similar manner as in FIGURE 2, but with the supercritical fluid added later. Supercritical fluid is added at the outlet of microwave transparent reactor 10 and not as the fluid being processed enters microwave transparent reactor 10. This configuration lowers the pressure inside the reactor D. The fluid then is pressurized and mixed with the supercritical fluid in secondary reactor 20 which is made of a high-pressure alloy. In reactor 20, solubilization of selected components takes place according to their solubility in the supercritical fluid at the pressure and temperature optimized for the specific fluid being processed. Secondary reactor 20 may contain similar static mixing elements as previously described. These elements function in the same manner as described in FIGURES 1 and 2. The process then continues to the separation tanks as described in FIGURES 1 and 2. The advantage of this variation is to optimize conditions for microwave energy absorption and supercritical fluid solubility without compromising either or being restricted by material components. These advantages will result in increased efficiency of the process and decreased cost of this embodiment of the system.

FIGURE 4 represents another variation of the present invention. In this variation, microwave energy is not needed for certain types of fluid. The microwave energy can be substituted with direct heating of the incoming fluids in secondary reactor 20, that is, a high pressure alloy reactor, to maintain constant temperature. The advantages of this feature are lower construction costs. While this embodiment is less flexible, it is viable and appropriate for specific applications.

The present invention combines two fluids (the fluid being processed and a supercritical fluid) at high pressure and achieves mixing by a device employing static mixing.

The purpose of this is to vigorously mix two fluids into essentially one homogenous suspension phase. This attribute is derived from the turbulence and the fluids' high linear flow velocity. When the fluids are no longer subjected to the turbulent mixing, the fluids will separate into individual components according to density and molecular weight and according to their solubility in the supercritical fluid. The insoluble and heavy material will settle out collecting in the bottom of the separation tanks. The solution of supercritical fluid, which includes dissolved components, will flow from the top of the first separation tank to another separation tank. One aspect of the present invention is that a series of tanks precisely calibrated for temperature and pressure create unique environments and will phase out higher molecular weight components in earlier tanks and progress to lighter components in subsequent tanks without pressurizing or expending additional energy.

Microwave energy is employed to breakup emulsions by both temperature and disruption of fundamental molecular forces. Temperature is not only necessary in controlling the conditions in the supercritical fluid section of the system 1 but is necessary in controlling conditions in separation tanks 12,14 and is integrated between both sections of the system 1.

Microwave energy is also used to accelerate reactions including but not limited to chemical and physical reactions. Synthetic combination, derivitization and phase separation is enhanced by the addition of microwave energy. Because of the variable nature of energy adsorption dependent on the polarity and dielectric nature of the sample components of the fluid being processed, a static mixer that provides for constant microwave energy absorption is used to place a constant of sufficient mass in the microwave and flow system. This is done to reduce the influence of the variability of the microwave energy absorbing nature of the fluid.

The union of both components into a single system is done in two different ways, with each having unique advantages. First, the mixing of the supercritical fluid with the fluid being processed may be performed as both enter the microwave energy field. Second, the microwave system is used as the initial system with the supercritical fluid flow being performed downstream thereof such that the efficiencies of each system are separate and in a sequential combination. That also permits a lower pressure microwave cell, increasing safety and reducing cost considerations. The chemical advantage of each variation determines the appropriateness of the approach. Certain specific process

conditions may require the simultaneous presence of the solvating power of the supercritical fluid. Other applications may reduce cost by using the second approach.

Another embodiment of the present invention includes the addition of an ultrasonication device. Ultrasonication in supercritical conditions can create sinusoidal compression/decompression waves inside the supercritical reactor. The advantage of this technology is to increase mixing strength to a maximum level extending to the molecular level.

EXPERIMENTAL RESULTS

Table 2

Used oil Starting Oil Co-flow Industrial Parameters Sample; Supercritical Specification
Tank 2 Microwave Furnace Fuel

Sample Processed Oil % Water 1.60% 0.30% 0.50% % Ash 0.85% 0.02% 0.95%

Flash point, F 200 200 > 120 Viscosity@122 F, cSI 43.79 42.1 < 50 AP ! Gravity, @60 F
27.8 26.1 25.9

Chlorine, in ppm 143. 3 0 < 0.2%

Sulfur, in ppm 0.456 0.322 < 1%

Data and specifications for an example of conventionally cleaned used oil processed using the co-flow supercritical microwave process of the present invention are illustrated in Table 2.

Industrial specifications for furnace fuel are also shown for comparison of the final product with these specifications. These results were analyzed by a commercial laboratory and are based on American Petroleum Institute (API) methods. The test setup was as shown in

FIGURE 2 and the process parameters were as follows: flow rate of fluid being processed: 1g/min, flow rate of supercritical fluid, CO₂ 10g/min, reactor temperature and pressure: 70 C, 500 psi, separation tank no. 1 temperature and pressure : 40 C, 500 psi, and separation tank no. 2 temperature and pressure: 25 C and 1,100 psi.

The present invention may be easily scaled with respect to flow and volume. Small systems may be placed on skids and used in remote locations. For example, a mobile system could be used to service a group of field deployed military vehicles. Small units may also be deployed on ships or other remote locations where the ability to recycle materials is critical. The system can be properly scaled and taken to locations where moderate quantities of materials to be recycled are stored.

The present invention may also be used in processes other than the purification of petroleum based products. The fields of application include many industries such as chemical environmental, food, medical, enzymatic, pharmaceutical and recycling.

The following paragraphs identify applications of the present invention in situations where components have differing solubilities. For example, the present invention can be used to purify azeotrope mixtures into their individual components, e. g. water and ethanol. Water solubility in supercritical fluid CO₂ is about 0.1%. This is in contrast with

very high solubility of alcohols under the same conditions of temperature and pressure. The separation of the alcohol/supercritical fluid solution from the water is performed easily in a cyclone separator which may be used in place of the previously disclosed static mixer. A similar system can be used to remove volatile organic compounds from water. Supercritical CO₂ can be mixed with water at various temperatures and pressures up to 1,000 atm to solubilize organic compounds.

There are many examples of the application of the present invention to solubility-based purification. For example, in the oil industry, the continuous production of clean and clear oil from used engine oil, a continuous separation of water and sludge from petroleum products, a continuous fractionation of gasoline/diesel mixture, and a continuous distillation of petroleum raw material into different products are all possible with the present invention.

The present invention also finds applications in the recycling of cooking oil and the recycling of ink. The pressure and temperature for each application is determined by the solubility parameters and phase equilibrium data for each component to be processed in the supercritical fluid. Other examples of applications of the present invention include a continuous extraction of fat from milk and dairy products, a continuous extraction of cholesterol from egg yolk, a continuous extraction of ethanol from fermentation broth, a continuous extraction and fractionation of butter oil, a continuous fractionation of glycerides, a continuous separation of enantiomers, a continuous fractionation of citrus oil and the production of flavinoids. Further examples of applications of the present invention include the continuous removal of heavy metals from nuclear industry waste. That can be accomplished by adding a detergent, to form micelles around the heavy metal ions. The micelles are then solubilized by the supercritical fluid thereby allowing them to be separated from the wastewater.

The following paragraphs identify applications of the present invention in situations where chemical reactions take place with the supercritical fluid. An example of this type of application of the present invention includes the treatment of sewage water with increased efficiency through a continuous supercritical water oxidation process. In this application, water and air can be mixed at a temperature and pressure above critical parameters of water (critical temperature 374 °C and critical pressure 216 atm). A continuous process by oxidation destroys organic compounds present at supercritical conditions and, in certain applications, requires sub-critical water to achieve similar results. Use of microwave or thermal energy to increase temperatures above critical parameters results in a destruction efficiency which exceeds 99.99%. The maximum temperature of the process can be reduced by the introduction of a catalyst such as MnO₂/CeO₂.

Another example of the application of the present invention is the continuous supercritical, or sub-critical, water oxidation of polychlorinated biphenyls with hydrogen peroxide. In this application, hydrogen peroxide and water are mixed and heated first to above 400 °C by microwave or thermal energy to produce hydroxyl radicals (OH). The mixture is then pressurized to above 250 atm. The temperature of the high pressure alloy

reactor is kept constant with conventional heating to insure 99% decomposition of most types of PCBs. Polymers, like fire retardants, can be oxidized in a similar process. The results from the oxidation process are environmentally acceptable substances. This process can also be used at different temperatures and pressures to insure maximum efficiency and oxidation of all types of polychlorinated biphenyls.

Other examples of applications of the present invention include a continuous supercritical water oxidation of alcohol distillery waste with hydrogen peroxide, a continuous supercritical water oxidation of phenyl, a continuous enzymatic synthesis of phenylethyl acetate and carbon dioxide, a continuous enzymatic esterification of alcohols, a continuous enzymatic synthesis of peptides, a continuous emulsion and dispersion polymerization of Nvinyl formamide in carbon dioxide, a continuous deacidification of vegetable oils, a continuous alkylation of isobutene in supercritical water, a continuous reaction of alkyl aromatics and supercritical water, a continuous hydrolysis of nitriles at sub-critical water conditions, a continuous cellulose decomposition in supercritical water and a catalyst, a continuous oxidation of methane into methanol with supercritical water, and the continuous photo-oxygenation of benzene in carbon dioxide.

The present invention is also applicable to processes based on chemical reactions, solubility and supercritical fluid anti-solvent recrystallization to produce fine particles and crystals. According to this application of the present invention, more than one component can be mixed to perform a chemical reaction followed by selective solubilization of supercritical fluids followed by fractionation at different supercritical conditions. The fractionated components can be crystallized online without spending additional energy by supercritical anti-solvent recrystallization. The initial reaction can take place with or without supercritical conditions. The separation of the reaction components can be based on different solubilities in the supercritical fluid. The production of the final crystal (powders) of the fractionated and purified products is done by sudden depressurization of the supercritical fluid solution into gas at the bottom outlet of the separation vessel. The dissolved material in the supercritical fluid undergoes nucleation and immediately forms crystals. The size and shape of the crystals can be controlled by the flow rate, the pressure drop rate and temperature. The pressure and temperature for each of the following applications is determined by the solubility parameters and phase equilibrium data for each component to be processed. A known computer simulation based on the modified equation of state (Bing-Robinson) can be used to predict the design parameters of the system at any scale to insure maximum efficiency of operation.

There are many examples of applications of the present invention under this category such as a continuous production of polymeric material under supercritical fluid conditions. Other examples of this process include using the monomer as the supercritical fluid in the production of, for example, polyethylene polymer from ethylene monomer. Supercritical anti-solvent recrystallization can be employed on line to produce fine powder of polymeric material. Other examples of applications of the process include a continuous production of fluoroether polyurethanes, a continuous production of impregnated polyurethylene, a continuous micro-coating of flavon with polymers, a

continuous production of polyurethane aerogels, a continuous production of powder coatings, a continuous fractionation of polymer products, and the production of amorphous pharmaceutical particles. Examples of use of the present invention for fractionation of many types of copolymers include using polypropylenepolyethylene copolymers to remove the low and high molecular weight fractions and the production of medical grade products of very high value on a continuous manner. The process can be used as a recycling process for polymeric rags and carpet. In this case the rag material is dissolved in solvent, and fractionation and crystallization using the present invention is performed. Other examples of applications of the present invention includes the continuous depolymerization of polymers and a continuous production of lipid-free human plasma products.

The present invention involves the continuous fractionation of any mixture of liquids, solutions, suspensions, azeotropes, and fluids into their individual components. The present invention is a continuous process where the fluids being processed are mixed with supercritical fluid in the presence of microwave and/or ultrasonication. The process is continuous and can handle numerous types of fluids to be processed because the process parameters are based on the material being processed as opposed to the contaminants. The process parameters have much larger values and appear as constants as compared to the contaminants. Thus, the present invention is less dependent on the analysis of the fluid being processed. The microwave energy will enhance the breakup of certain emulsions or speedup chemical reactions. Static mixing is used to provide massive turbulence, which yields extensive mixing in a short period of time on a continuous basis enhancing the solvation reactions without the need for massive high pressure batch vessels. The ultrasonication will speed up solubility of specific components in supercritical fluids. The dissolved components are carried away from the undissolved components by the supercritical fluid and can be fractionated into individual components according to their solubility in supercritical fluid at specific temperature and pressure. The supercritical fluid is then recycled and used in a close loop system.

The present invention depends more on the fundamental solubility differences of the remaining valuable key components than on the contaminant wastes that have been introduced and is therefore more fundamental and generally applicable. The water, sludges, residual metal components and other polar components or the waste oils do not determine the process. Rather the inherent solubility of the oil molecules to be recovered determines these conditions making this process more fundamentally robust and generally applicable.

While the present invention has been described in conjunction with preferred embodiments thereof, those of ordinary skill in the art will recognize that many modifications and variations may be made. The following claims are intended to cover all such modifications and variations.

Claims

WHAT IS CLAIMED IS: 1. A method of processing a fluid, in which the first two steps may be performed in any order, comprising: mixing a fluid to be processed with a supercritical fluid to dissolve at least one component in the fluid to be processed; applying microwave energy to at least the fluid to be processed; allowing undissolved components to settle; and separating the dissolved component from the supercritical fluid.

2. The method of claim 1 wherein said mixing step includes the step of statically mixing.

3. The method of claim 1 additionally comprising the step of adding sonic energy during said mixing step.

4. The method of claim 1 wherein the supercritical fluid is selected from a group consisting of CO₂, H₂O, N₂O, NH₃, n-C₅, n-C₄, SF₆, Xe, CCl₂F₂ and CHF₃.

5. The method of claim 4 additionally comprising the step of adding a solvent to modify the solubility of the supercritical fluid.

6. The method of claim 1 additionally comprising the step of recycling said supercritical fluid.

7. A method for recycling a reusable oil from a waste material comprising: statically mixing said waste material with a supercritical fluid to dissolve oil from the waste material; applying microwave energy to said mixed fluids; allowing undissolved components to settle; and separating the dissolved oil from the supercritical fluid.

8. The method of claim 7 wherein said steps of statically mixing and applying microwave energy are performed substantially simultaneously.

9. The method of claim 7 additionally comprising the step of adding sonic energy during said statically mixing step.

10. The method of claim 7 wherein the supercritical fluid is selected from a group consisting of CO₂, H₂O, N₂O, NH₃, n-C₅, n-C₄, SF₆, Xe, CCl₂F₂ and CHF₃.

11. The method of claim 10 additionally comprising the step of adding a solvent to modify the solubility of the supercritical fluids.

12. The method of claim 7 wherein said step of allowing includes the step of allowing water and sludge to settle.

13. The method of claim 7 additionally comprising the step of recycling said supercritical fluid.

14. A method for recycling a reusable oil from a waste material comprising: applying microwave energy to said waste material; pressurizing said waste material and statically mixing said waste material with a supercritical fluid to dissolve oil from the waste material; allowing undissolved components to settle; and separating the dissolved oil from the supercritical fluid.
15. The method of claim 14 additionally comprising the step of adding sonic energy during said pressuring said waste material and statically mixing step.
16. The method of claim 14 wherein the supercritical fluid is selected from a group consisting of CO₂, H₂O, N₂O, NH₃, n-C₅, n-C₄, SF₆, Xe, CCl₂F, and CHF₃.
17. The method of claim 14 additionally comprising the step of adding a solvent to modify the solubility of the supercritical fluids.
18. The method of claim 14 wherein said step of allowing includes the step of allowing water and sludge to settle.
19. The method of claim 14 additionally comprising the step of recycling said supercritical fluid.
20. A method of processing a fluid, comprising: statically mixing said fluid with a supercritical fluid to dissolve at least one component in the fluid to be processed ; applying thermal energy; allowing undissolved components to settle; and separating said dissolved component from said supercritical fluid.
21. The method of claim 20 wherein said steps of statically mixing and applying thermal energy are performed substantially simultaneously.
22. The method of claim 20 additionally comprising the step of adding sonic energy during said statically mixing step.
23. The method of claim 20 wherein the supercritical fluid is selected from a group consisting of CO₂, H₂O, N₂O, NH₃, n-C₅, n-C₄, SF₆, Xe, CCl₂F₂ and CHF₃.
24. The method of claim 20 additionally comprising the step of adding a solvent to modify the solubility of the supercritical fluids.
25. The method of claim 20 wherein said step of allowing includes the step of allowing water and sludge to settle.
26. The method of claim 20 additionally comprising the step of recycling said supercritical fluid.
27. An apparatus for processing a fluid, comprising: a reactor comprising static mixing elements for mixing said fluid to be processed and a supercritical fluid, said reactor being

transparent to microwave energy; a microwave energy source configured to supply microwave energy to said reactor; and at least two separation vessels.

28. The apparatus of claim 27 additionally comprising an ultrasonication device configured to supply sonic energy to said reactor.

29. The apparatus of claim 27 additionally comprising a recycling system configured to recycle said supercritical fluid from said at least two separation vessels.

30. An apparatus for processing a fluid, comprising: a microwave energy source configured to supply microwave energy to said fluid to be processed; a reactor comprising static mixing elements for pressurizing and mixing said fluid to be processed and a supercritical fluid; and at least two separation vessels.

31. The apparatus of claim 30 additionally comprising an ultrasonication device configured to supply sonic energy to said reactor.

32. The apparatus of claim 30 additionally comprising a recycling system configured to recycle said supercritical fluid from said at least two separation vessels.

33. An apparatus for processing a fluid, comprising: a reactor comprising static mixing elements for mixing said fluid to be processed and a supercritical fluid, said reactor being transparent to thermal energy; a thermal energy source configured to supply thermal energy to said reactor; and at least two separation vessels.

34. The apparatus of claim 33 additionally comprising an ultrasonication device configured to supply sonic energy to said reactor.

35. The apparatus of claim 33 additionally comprising a recycling system configured to recycle said supercritical fluid from said at least two separation vessels.

36. A continuous process for recycling waste oil, the improvement comprising determining the process parameters based on the oil to be recovered instead of the contaminants in the waste oil.

37. A method for continuously processing a fluid, the improvement comprising determining the process parameters based on the solubility of at least one component of the fluid to be processed instead of on the components to be removed from the fluid to be processed.